Combustion Research Facility News

Volume 20, No. 1 January/February 1998 Sandia National Laboratories

New thermal de-NO_x model developed

Jim Miller and Peter Glarborg (Technical University of Denmark) have formulated a chemical kinetic model for the Thermal De-NO_x process (NO removal by ammonia addition) that predicts the NO removed and the N_2O and NO_2 produced by the process over a range of temperatures and initial oxygen concentrations. The new feature of the mechanism is that NO_2 appears as an essential intermediate in the reaction scheme. It is formed as a consequence of NNH, produced from the NH_2 + NO reaction, reacting with molecular oxygen,

$$NNH + O_2 \leftrightarrow N_2 + HO_2$$
$$HO_2 + NO \leftrightarrow NO_2 + OH,$$

and is converted back to NO by

$$NH_2 + NO_2 \leftrightarrow H_2NO + NO,$$

followed by $H_2NO \leftrightarrow HNO \leftrightarrow NO$. Nitrous oxide is produced by two different reactions,

$$NH_2 + NO_2 \leftrightarrow N_2O + H_2O$$

and

$$NH + NO \leftrightarrow N_2O + H.$$

The first is the primary source at relatively high oxygen concentrations and the second is dominant for low O_2 levels. The lifetime of NNH employed is $\tau_{NNH} = 10^{-7}$ sec, which is less than the upper limit set by experiment but still larger than the best theoretical prediction.

In modeling flow-reactor experiments for the Thermal De-NO_x process, Jim and Peter discovered that the temperature at which NO removal begins for any initial gas composition is determined completely by the mix of chain termination and chain branching processes that take place. In general, this initiation temperature is determined by the branching fraction (α of the NH_2 + NO reaction,

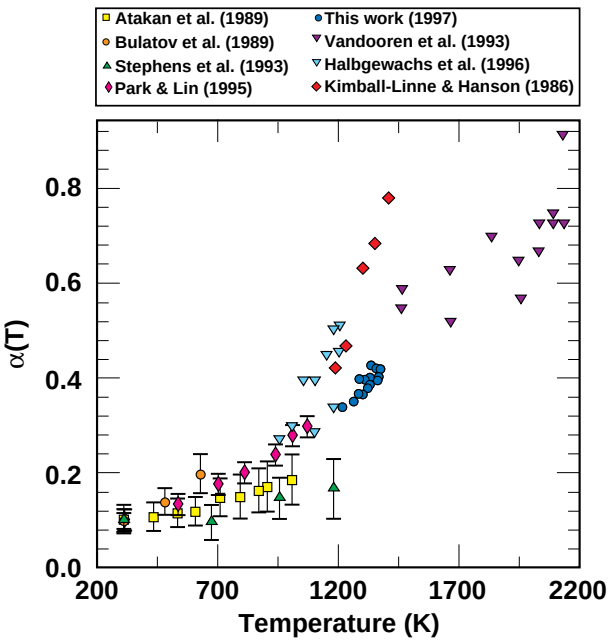
$$NH_2 + NO \rightarrow NNH + OH \qquad (1a)$$
$$\rightarrow N_2 + H_2O, \qquad (1b)$$

where $\alpha = k_{1a}/(k_{1a} + k_{1b})$, the competition for NNH between reactions (2) and (3)

$$NNH \rightarrow N_2 + H \qquad (2)$$
$$NNH + O_2 \rightarrow N_2 + HO_2, \qquad (3)$$

and various reactions that occur as a consequence of reaction (3). At sufficiently low oxygen levels (~0.1%), reaction (3) cannot compete with (2) and NNH always dissociates. Under such conditions the initiation temperature depends almost exclusively on α.

Jim, Peter, Per Kristensen, and Kim Dam-Johansen (both also of the Technical University of Denmark) have used this information to determine the branching fraction from carefully selected flow reactor experiments on $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ mixtures. The results show that α increases gradually from a value of 0.35 ± 0.04 at 1211 K to 0.45 ± 0.02 at 1369 K. The uncertainty in these values is due primarily to the influence of secondary reactions whose rate coefficients are relatively well known. The data blend smoothly with the most recent direct measurements and confirm the significant rise in branching fraction with temperature suggested by previous high temperature determinations in static reactors and flames. The figure below shows the data for $\alpha(T)$.



Advisory Board meets

The CRF Advisory Board was convened by Tom Hunter, Vice President Sandia/California, and Bill McLean, Director of the Combustion and Physical Sciences Center, on November 6 and 7 to discuss the CRF Phase II construction project and future program directions in combustion research. For more information on the Advisory Board's discussions and a photo of the Board, see the December What's *HOT* at the CRF on the CRF Website at http://www.ca.sandia.gov/CRF; more information on CRF Phase II is also available there.

The CRF recently hosted two visitors from VTT Energy, Jyväskylä, Finland, to discuss potential collaborative work on combustion of biomass, black liquor, and coal for power generation. Shown in the photo are Don Hardesty, Seppo Viinikainen (VTT, Research Manager), Mikko Kara (VTT, Research Director), Larry Baxter, and Chris Shaddix.

Scott Sinquefield (right), Oregon State University, recently completed his doctoral research experiment with Larry Baxter (left). Scott is investigating combustion and ash deposition behavior of black liquor, a fuel produced in the process of pulp and paper manufacturing. Black liquor boilers represent the single largest capital investment in a pulp mill, and ash deposition is one of the largest operational problems associated with these boilers. Scott's work quantified mechanisms and rates of fume particle deposition during the combustion of black liquor. Scott and Larry are discussing an ash deposit generated in the Multifuel Combustor.

Mike Westley (center), a student of Professor Paul Houston of Cornell, visited the CRF this summer to work with Dave Chandler (left) and postdoctoral fellow Tom Lorenz (right) on imaging of bimolecular reactions.

The CRF News is published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.
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International Conference on Chemical Vapor Deposition

Mark Allendorf led a nine-member U.S. organizing committee for the 14th International Conference on Chemical Vapor Deposition (CVD) held at the Palais de Congress in Paris, France, during the first week of September, 1997. The conference was part of The Electrochemical Society's 192nd meeting. It was also held jointly with the EUROCVD-11 meeting for the first time and involved high-level cooperation between the U.S. organizing committee and the EUROCVD governing board.

More than 240 papers were presented, which brought together scientists from nearly every country in Europe plus the U.S., Canada, and the Far East, making it the largest of these conferences ever held. Due to the overwhelming success, the U.S. and EUROCVD groups have pledged to continue their cooperation in organizing future meetings.

The meeting included nine sessions on topics such as fundamental chemistry of CVD processes, modeling, diagnostics for process control, and deposition of hard coatings, electronic materials, and ceramics. A 1600-page proceedings volume was published and is available from The Electrochemical Society (http://www.electrochem.org).

Fuel property effects on diesel spray penetration studied

The effect of fuel volatility on the liquid-phase fuel penetration in a direct-injection (D.I.) diesel engine has been recently investigated by a team consisting of Robert Canaan, John Dec, Robert Green, Eldon Porter, and Dan Daly (Lubrizol Corp.), with funding support provided by the Lubrizol Corporation. The objective of this work was to characterize liquid-fuel-jet penetration and evaporation for a variety of diesel fuels under realistic diesel engine operating conditions.

The rate and extent to which the injected liquid-fuel jet penetrates across the diesel engine combustion chamber is an excellent indicator of how the evaporative process occurs under a specified set of operating conditions. Also, the development of the liquid-fuel jet has an important influence on air utilization and fuel-air mixing, which directly impact engine performance and emissions levels.

Using the optically accessible Sandia-Cummins heavy-duty D.I. diesel engine (*CRF News* **15**:3), researchers measured liquid-phase fuel penetration for a total of eight diesel fuels using laser elastic-scatter imaging. The experiments were conducted at a medium speed (1200 rpm) operating condition with a motored TDC (top dead center) temperature and pressure of 992 K and 5.0 MPa, which are representative diesel conditions.

The resulting data show that the liquid fuel initially penetrates almost linearly with increasing crank angle until reaching a maximum characteristic length, beyond which effectively all of the diesel fuel has been vaporized. This can be seen in Figure 1 for four of the fuels tested, which include a complex diesel parent fuel and three fuel fractions distilled from the parent fuel.

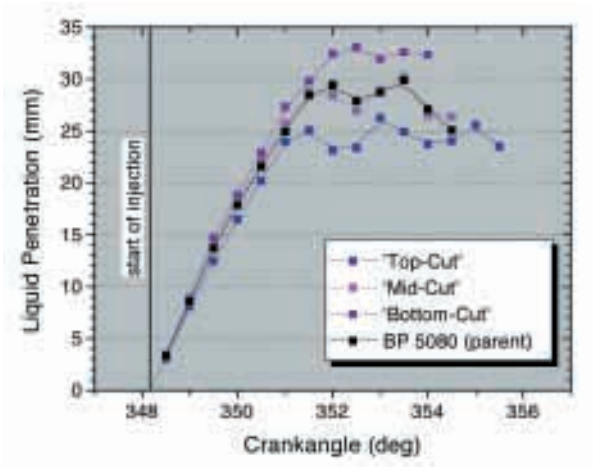


Figure 1. Liquid-phase fuel penetration for a complex diesel fuel (BP 5080) and three distilled fractions of the parent fuel designated 'Top-Cut' (lightest), 'Mid-Cut' (middle), and 'Bottom-Cut' (heaviest fraction). Data are averaged over 12 cycles. Note that the parent fuel behaves most like the middle fraction.

Figure 2 shows typical elastic-scatter images of the liquid-fuel jets after the jets have reached their maximum characteristic length. These cycle-resolved images were obtained through the piston window and correspond to the fuel types seen in Figure 1 at a crank angle of 352.5˚ (0˚ = TDC intake). For all fuels tested in this engine, liquid-fuel wall impingement did not occur, even for the relatively low volatility fuels.

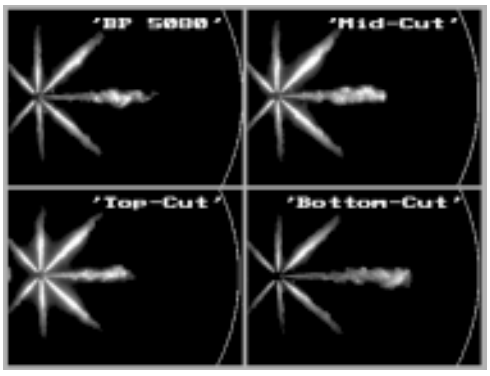


Figure 2. Typical maximum liquid-phase fuel penetration for the BP 5080 parent fuel and its three distilled fractions. Representative cycles are shown at a crank angle of 352.5˚. Only the fuel jet in the 3 o'clock position is fully illuminated by the laser sheet. The curve at the right of each image indicates the edge of the combustion bowl.

The data also show that the maximum liquid-fuel penetration is strongly influenced by fuel volatility. Specifically, there is a strong positive correlation (roughly linear) between maximum liquid penetration and fuel mid-boiling point, as shown in Figure 3 for the eight diesel fuels used in this study. This strong correlation indicates that under diesel conditions, maximum liquid-fuel penetration is heavily dependent upon the evaporative process.

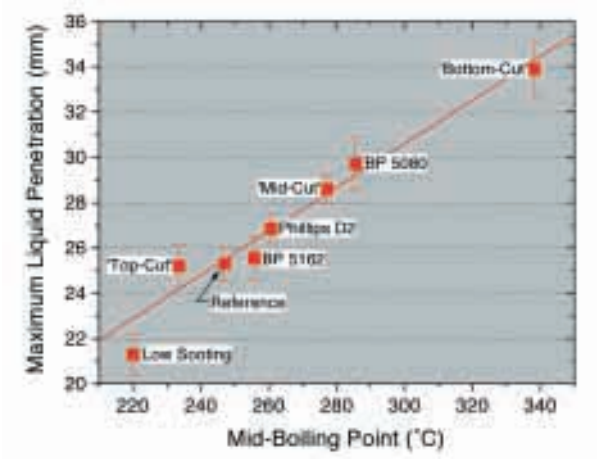


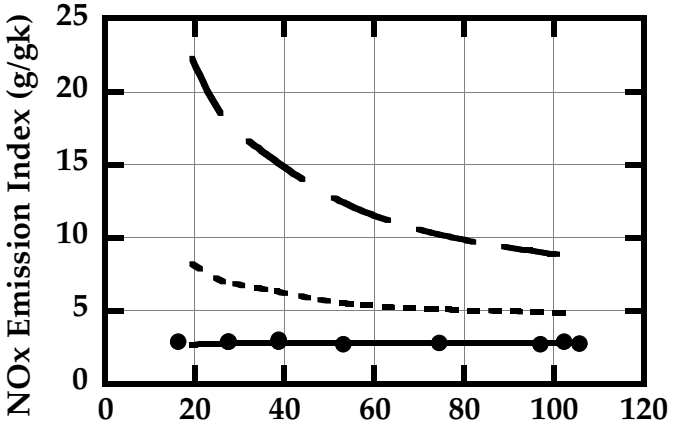
Figure 3. Maximum liquid-phase fuel penetration for all fuels tested correlated with fuel mid-boiling point.

The results of this collaborative research are leading to improved computer model development and the ability to manufacture fuels and engines that continue to meet tightening emissions standards without sacrificing performance.

TSL models kinetics in turbulent jet flames

The ability to predict pollutant emissions from turbulent jet flames is an important step towards using models to design burners. Unfortunately, the detailed chemical kinetic mechanisms necessary to describe pollutant formation are too large to fit in conventional turbulence models. As an alternative, Andy Lutz and Gene Broadwell (Consultant), working under support of the Gas Research Institute (GRI), developed the Two-Stage Lagrangian (TSL) model to simulate detailed kinetics in turbulent jet flames.

The two-stage approach, originally developed by Broadwell at Caltech, is based in the experimental observation that reactions occur first in diffusion layers and continue in regions that are nearly homogeneous, created by turbulent mixing. The homogeneous regions are represented by one perfectly stirred reactor. The diffusion layers can be represented by either a one-dimensional, strained diffusion flame, or more simply, a second perfectly stirred reactor. While the reactor/flame version may seem more sophisticated, the two-reactor model yields essentially the same results, at greatly reduced computational expense, so the majority of applications use the two-reactor version.



NO_X emissions index (defined as grams of NO_X generated per kilogram of methane) for methane flames with varying jet velocity. Long-dashed curve is adiabatic flame with constant momentum; short-dashed curve includes buoyancy; solid curve includes radiation loss. Data provided by Turns.

As an example of the TSL model performance, the figure shows a comparison of computed NO_X emissions from methane flames to measurements of Stephen Turns (Penn State). The three curves show the importance of including the entrainment rate for buoyant flow and the energy loss of flame radiation, which is adjusted to the measured radiant fraction.

The unique feature of the model is the simple, yet physically based representation of turbulent mixing. The model represents the mixing rate and momentum transport by empirical correlations, allowing use of a detailed chemical kinetic mechanism, such as GRI-mech (250 reactions involving 50 species), in a computation that takes only minutes on a personal computer. The program runs as a CHEMKIN application, providing a convenient tool for including any elementary reaction mechanism. The TSL model will appear soon in *Combustion and Flame*, and also as an option in the GRI-mech web-page calculator (http://euler.berkeley.edu/gri_mech).

CRF Phase II Team wins Turquoise Award

In the fifth annual Sandia President's Quality Award (PQA) process, the CRF II Project Team was among the Turquoise Award winners. This prestigious award was presented via live videolink from Albuquerque on October 29. California Laboratory Vice President Tom Hunter said in honoring the California winners: "...the world is a competitive place....effective teamwork is no longer an option; it is, in fact, essential. Our customers deserve and expect nothing less."

The team comprises John Beitia, Bob Gallagher, Lee Gardizi, Jake McMichael, Jamie Morris, Hal Norris, Don Putz (CRF II project manager), and Howard Royer. The PQA is based on the Malcolm Baldrige National Quality Award criteria and principles.

See the CRF Website (http://www.ca.sandia.gov/CRF), What's *HOT* at the CRF and CRF Phase II for more information.

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